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REPORT

On

International Conference on "Innovative /Cost-effective Materials Processing Methods -Films & Nanocrystalline Powders"

6th and 7th July 2000 at Imperial College, London.

CONTENTS

Keywords

Innovative, cost-effective, materials processing methods, films, coatings, nanocrystalline powders, process-structure-property relationships

The 1st International Conference on "Innovative/Cost-effective Materials Processing Methods (**ICMPM**)" was organised by Dr. K. L. Choy, Department of Materials, Imperial College of Science Technology and Medicine, London in collaboration with the Structural of Materials and Surface Engineering Committees of The Institute of Materials. The conference was sponsored by the *Office of Naval Research International Field Offices (ONRIFO).*

1. Welcome address by the organiser and summary

On 6^{th} July 2000, Dr.K.L.Choy welcomed over 35 delegates from 10 countries including UK, USA, France, Germany, Switzerland, Denmark, Poland, the Netherlands, Russia, Spain to ICMPM conference at Imperial College. The venue was held at the Dept of Materials in the Royal School of Mines. This was followed by an official welcome addressed by the Dean of the Royal School of Mines, Prof. John Kilner.

As the use of advanced engineering ceramic films and powders for structural and functional applications is expanding rapidly. Improved materials and innovative methods of fabrication are needed to enhance the engineering performance and reduce the production costs. Therefore the aim of the ICMPM conference was to bring together international engineer and material scientists concerned with the innovative/cost-effective materials processing methods, at a mature production stage and also in development. Issues and strategies associated with scaling-up were also highlighted. Modelling of deposition techniques and properties were also presented. Advanced on-line/in-situ process monitoring techniques were reported by several speakers. Ten invited papers and seven posters covering a wide variety of novel and/or cost effective synthesis of nanoparticles, films and their applications were presented and discussed. The poster session had facilitated informal discussions between the authors and conference delegates.

2. Technical Contents

Oral presentation

6th July 2000

2.1. Flame Aerosol synthesis of titania (Invited paper)

Prof. Sortiris E.Pratsinis from ETH, Zurich had highlighted the use of flame aerosol synthesis as a cost-effective method to synthesis nanoparticles of titania. The growth of the nanoparticle was closely monitored by sampling the particles using the thermophoretic method for subsequent particle size measurement using TEM. The deposition temperature was determined using Fourier Transform Infrared Spectroscopy. The flame aerosol synthesis method has produced titania with a particle size distribution of 5-50 nm and a standard deviation of less than 1.45. The role of particle sintering and surface reactions during synthesis process was discussed.

2.2 CCVD –Low cost vapour deposition of thin films in the open atmosphere (Invited paper)

Dr. Hunt of Micro Coating Technologies Inc, U.S.A explained the state-of-the-art on the preparation of thin film at a low cost using a patented technique called Combustion Chemical Vapour Deposition (CCVD) technique. During the CCVD process, the chemical precursors are dissolved in organic/combustible solvent. The resultant solution is atomised using Nanomiser^{TM} into submicron droplets, which are subsequently carried using an oxidising gas into a flame where they undergo combustion and pyrolysis to deposit a thin film onto a substrate. The process can be performed in open atmosphere and does not require expensive equipments or vacuum systems. This method has been patented for applications other than diamond coatings, for example, a wide range of inorganic thin films, mostly oxides, onto metal, ceramic or plastic substrates. Potential applications in the fabrication of corrosion resistant, electronic and optical coatings were presented.

2.3. Nano particles synthesis in sodium halide jet flames (Invited paper)

Prof. Alexbaum of Wasington University, explained the fabrication of metal and non oxide nanoparticles by sodium halide flames. Conceptually, this process is similar to the commercial flame synthesis process for the ceramic oxide and carbon black powder. The only difference is that this process employs a unique encapsulation

process during the aerosol growth stage to control the size of the particles, minimise agglomeration and protects the powders from oxidation/hydrolysis during post-synthesis handling. The encapsulation material (typically salt) can be removed during post flame processing. The experimental results and Monte Carlo numerical simulation of the encapsulation process were presented for the synthesis of non-oxide powders (sizes from 2-1000 nm) such as Ti, W, Al, Ta, TiB_2, AlN and TiN using both laminar and turbulent jet flames.

2.4 Electrostatic spray assisted vapour deposition (ESAVD) of coatings and films (Invited paper)

Dr.K. L. Choy from Imperial College has developed a novel and cost-effective coating method called Electrostatic spray assisted vapour deposition (ESAVD). This method involves spraying atomised precursor droplets across an electric field where the droplets undergo chemical reaction in the vapour phase near the vicinity of the heated substrate. This produces a stable solid film. The process is conducted in an open atmosphere; it is rapid, simple and flexible as compared to the CVD and PVD processes. It is also capable of coating complex shaped components. The process-structure-property relationships were discussed. The potential of the process for producing thin and thick films for commercial applications such as thermal barrier coatings for aerospace and power generation applications, functional thin films for electrical and electronics, automotive, chemical industry, and biomedical sectors has been highlighted.

2.5 Directed vapour deposition (DVD) of electron beam evaporant (Invited paper)

Dr.Groves of University of Virginia presented the use of directed vapour deposition(DVD) approach to deposit coatings. DVD uses a focussed vapour stream and low vacuum e-beam evaporation as compared to the high vacuum use in the conventional e-beam evaporation method for the rapid and efficient film deposition. The mechanism of gas and vapour transport in the DVD system were examined experimentally through the luminescene from the vapour in the system, as well as through the use of Direct Simulation Monte Carlo, bimolecular collision theory codes and vapour transport models. The microstructural control of the DVD process could be enhanced by coupling plasma activation of the gas and vapour stream prior to the

deposition. The suitability of the DVD method to deposit columnar thermal barrier coatings with porous microstructure for potential use in gas turbine applications was highlighted.

2.6 Synthesis of nanopowders by microwave plasma process. Perspective for process up scaling. (Invited paper)

Prof. D. Vollath, Karlsruhe University has developed the use of microwave plasma process to produce non-agglomerated nanosized powders because the produced particles leave the plasma zone with electric charges of the same sign. In addition, this new process also allows the coating of nanosized particles in the second step of production by lowering the reaction zone temperature to as low as 150°C for ceramic, polymer or carbon coating. Such coated particles can be used as starting materials for the fabrication of homogeneous composites. Both oxide and non oxide (e.g. nitride, sulphide or selenide) nanoparticles (5-20nm) have been fabricated using this method. The issues related to process scale-up were addressed and a demonstration plant capable of producing 100 g batches was presented.

2.7 Hypersonic plasma particles deposition of nanocrystalline coatings (Invited paper)

Prof. S.Girshick, University of Minnesota, USA presented a method of depositing nanocrystalline coatings using a hypersonic plasma particle deposition (HPPD) method. In this process, gaseous reactants are injected into thermal plasma, which is then expanded through a nozzle, with the pressure dropping from sub-atmospheric to about 2 Torr. The resulting sharp temperature drop drives the nucleation of nanoparticles, these particles are accelerated by a highly supersonic flow and then deposited by continuous film deposition or focused beam deposition. Various coatings such as SiC, TiC and layered Ti/TiC composites for potential applications as wear and friction resistant coatings have been deposited using this process. The microstructure and properties of the coatings were presented. The typical grain sizes of the coatings are ~20nm, close to the particle sizes measured in the aerosol jet downstream of the nozzle.

2.8 Chemical Vapour Synthesis of nano crystalline powders, ceramics and coatings (Invited paper)

Prof. H.Hahn from Darmstadt University presented the use of Chemical Vapour Synthesis (CVS) method for the fabrication of nanoparticles with smaller particle size, narrower size distributions, good crystallinity and reduced degree of agglomeration than most other techniques. The potential of CVS to produce oxide nanopartciels, homogenous coatings and coatings with a gradient of porosity or composition was presented. The elemental distribution within the nanoparticles could be varied to alter the properties of the nanoparticles. Sintering, mechanical and optical properties of the nano particles were also discussed.

2.9 Application of pulsed injection MOCVD to the deposition of oxide single layers and super lattices (Invited paper)

Prof. Senateur of LMPG, ENS de Physique de Grenoble explained a novel liquid precursor delivery and vapour generation method based on pulsed injection for the MOCVD process. The pulsed injection method uses fuel injection principles in thermal motors. It involves a sequential injection of microamounts (i.e. few mg) of organometallic precursor solution into an evaporator, where a flash volatilisation occurs. The thickness of the layer, coating stoichiometry and the growth rate can be controlled precisely (digital growth) using the pulsed injection MOCVD. This is especially important for the synthesis of superlattice and multilayers with complex stacking at nanometer scale level or the study of variation of stoichiometry on the properties of materials. For example $SrTiO_3$/ $YBa_2Cu_3O_7$ double layer, $YBa_2Cu_3O_7/PrBa_2Cu_3O_7$ multilayers, crystallised Ta_2O_5/amorphous SiO_2 for optical guides, antireflective layer applications, as well as $(La,Sr)MnO_3/SrTiO_3$ superlattices with various modulation length have been deposited on single crystal substrates.

2.10 From diamond particles to nanocrystalline diamond coatings (Invited paper)

Stanislaw Mitura of Lodz University, Poland explained the use of Radio Frequency Plasma Chemical Vapour Deposition (RFPCVD) for the synthesis of diamond particles and nanocrystalline diamond coatings. The effects of process parameters such as negative self biased potential and hydrocarbon pressure on the substrate

temperature and total energy transferred from plasma to the layer during deposition, and hence the properties of the layers (e.g. energy gap, optical absorption and refractive index and hardness) were presented. During preparation of diamond films self bias potential, hydrocarbon pressures of the reaction temperature of the substrate are all important. The applications of nanocrystalline diamond coatings for surgical appliances and decorative fields such as medals etc. were also highlighted.

2.11 A novel method of applying metal coatings on powders and substrates

Fokina et al from St Petersburg University explained the use of solid-phase reactions through milling at low heating temperatures (e.g. 200-500°C) in a low pressure (e.g. 10^{-3} mmHg) or inert atmosphere for the fabrication of metal coatings onto powders and substrates. Cu, Ti, Al, Ni, Au and Ag coated powder materials (e.g. SiC, BN, glass and metals) were prepared using this low cost technique. The potential of this technique for producing metallisation of abrasive grains in manufacture of abrasive tools, and metal matrix composites was discussed.

3. POSTERS

3.1 Processing and characterization of doped nanocrystalline tetragonal zirconia as potential new solid electrolytes

Boulc'h Florence et al, INPG-CNRS France explored the used of zirconia doped with yttria, scandia or gadolinia to form tetragonal zirconia with the aim to improve the electrical property of the oxide so that it can provide improved solid electrolyte for solid oxide fuel cells operating at about 750°C, with better thermal and mechanical properties than the cubic phase. These materials were prepared in the form of nanocrystalline powder by spray pyrolysis using an ultrasonic mist generation method to produce the aerosol. The aerosol was delivered into a tube furnace maintained at 600°C. The produced powder was subsequently sintered to produce ceramics with grain size in the range of 6-100 nm. Scandia doped zirconia exhibited the highest conductivity.

3.2 Atmospheric pressure plasma surface treatment of ceramic filter material

Ba Duaong Phan of UMIST and EA Technology has explored the use of a novel atmospheric pressure non equilibrium plasma (APNEP) process to improve the surface properties of the ceramic used to manufacture the filters for corrosive raw waste incineration flue gas applications. The potential of the APNEP for filter treatment and to design coating to arrest clogging of fine particles from flue gas was discussed. The flow field, heat transfer of the turbulent plasma jet and particle tracking have been investigated numerically to predict the surface coating layer profile and compared with the coated ceramic surfaces which were characterised experimentally.

3.3 Shallow ion implantation in plasma assisted surface engineering.

Sokoowska et al from Poland investigated the process parameters that influence the diffusion process that occur during the ion assisted chemical reactions of diamond like carbon films, nanocrystalline diamond films and high alloy steel. The shallow implantation of ions (which are accelerated within the neighbouring to electrode region of the potential drop) that occur in plasma environment activates the diffusion process.

3.4 Structural and electronic properties of carbon rich a-SiC films

Aleksander Werbowyn et al from Warsaw University of Technology, Poland described the structural and electronic properties of carbon rich amorphous SiC (a-SiC) films deposited on Si substrates by sputtering in plasma of SiC target. a-SiC layers have potential applications as an active as well as passive (e.g. protective and passivation coatings) components in solar cells, light emitting diodes or photodetectors. The effect of process parameters such as pressure, reagent and discharge voltage on the properties of the films were also presented and the optimum process parameters for the deposition of a-SiC layer with the desired structural and electrical properties were established.

3.5 Directed Vapour Deposition (DVD) of Electron beam evaporant

In addition to the invited talk, James Groves (University of Virginia) also presented a poster on DVD of electron beam evaporant to describe the process in detailed. The

use of plasma activation of the gas and vapour stream prior to deposition to enhance DVD's ability to vary deposit microstructure was highlighted further in the poster.

3.6 C-axis texturing of ZnS thin films on glass substrate

M. Wei and K.L Choy (Imperial College) explained the preparation of ZnS films using electrostatic spray assisted vapour deposition (ESAVD) technique. The process principle and versatility of the ESAVD technique was given in the invited talk. This poster highlighted further the capability of ESAVD to produce oriented films onto amorphous substrates using the example of c-axis texturing of ESAVD deposited ZnS thin films on glass substrates as confirmed from XRD pole figure and TEM characterisation. The unique texture formation mechanism was explained.

4. Panel Discussion

Panel discussion was held at the end of each day of the conference to provide a forum for debate, discussion on papers presented on that day and opportunities for exchange of ideas.

The panel discussion on 6th July was chaired by Profs. Dieter Vollath and Horst Hahn. The important aspects discussed were

Nanocrystalline powders

- various novel methods of synthesising nanocrystalline powders such as flame aerosol synthesis, sodium/halide jet flames, microwave plasma process were discussed and compared.
- the morphology and microstructure of nanosized particles
- methods to avoid agglomeration
- process modelling and simulations
- on-line particle measurement techniques and characterization
- potential industrial applications seems to be limited to functional applications rather than structural applications where technology can outweigh the cost of production.
- health and safety of handling and storing of ultrafine powders

Coatings and films

• various novel coating methods such as CCVD, ESAVD, DVD and HPPD were discussed. The potential of these techniques to provide cost-effective ways to produce coatings at higher deposition rates and/or new structures as compared to the existing methods were discussed.

The panel discussion on 7th July was chaired by Profs. James Groves and Axelbaum

- Other improved methods of producing coatings such as CVS, pulsed injection MOCVD and RFPCVD and their applications were discussed.
- general issues related to exploitation and commercialisation of these innovative and/or cost-effective methods were discussed.
- the formation of start up companies and issues related to the intellectual property rights to protect the invention and technologies were discussed.
- It was felt that the a follow up conference along the theme of this conference should be encouraged. However, more participation from various manufacturing companies are essential and sessions should be included to allow representatives from commercial companies to express the industrial and market needs and give advice on ways to exploits these novel processing methods.

The weather was kind in London during the conference and a full social program complemented the scientific event on 6th July evening with a dinner at Polish Club, London. Some of the interested guests toured the laboratory facilities at the Materials Department, Imperial College on the 7th July.

Dr.Choy proposed a vote of thanks on the evening of 7th after panel discussion.

5. Conclusions

It was felt that the conference was timely as the surface engineering providers and manufacturers are under immense pressures to reduce the cost of production and yet maintained and/or improved the quality of the products. The invited talks presented at the conference highlighted various innovative and/or cost-effective processing

methods for nanocrystalline powders, thin films or thick coatings. These methods have the potential to revolutionise the existing materials fabrication methods by providing cost-effective alternatives, processes with improved efficiency and/or product with improved quality. A followed up conference has been suggested to capture the essence of such conference theme with more industrial participation.

6. Acknowlegements

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- the sponsor ***ONRIFO***, especially Dr Phillip A. Parrish, Associate Director of Material Science and Engineering, Office Of Naval Research International Field office, for the financial support and encouragement to consider organising a follow up meeting.
- the Centre for Continuos Education, Imperial College, especially Ms Hersha Mistry (Conference co-ordinator) for ensuring the smooth running of the conference.
- the Prof Kilner, the Dean of Royal School of Mines, Imperial College for giving the official opening remark and supporting this conference.
- Jim Wright, Chandra and Ming Wei for providing valuable assistance at the conference.

Finally special thanks go to all invited speakers, participants and delegates who attended and supported the conference and made it happened!